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Hierarchical responses of soil organic and inorganic carbon dynamics to soil acidification in a dryland agroecosystem, China

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Abstract: Soil acidification is a major global issue of sustainable development for ecosystems. The increasing soil acidity induced by excessive nitrogen (N) fertilization in farmlands has profoundly impacted the soil carbon dynamics. However, the way in which changes in soil pH regulating the soil carbon dynamics in a deep soil profile is still not well elucidated. In this study, through a 12-year field N fertilization experiment with three N fertilizer treatments (0, 120, and 240 kg N/(hm^2•a)) in a dryland agroecosystem of China, we explored the soil pH changes over a soil profile up to a depth of 200 cm and determined the responses of soil organic carbon (SOC) and soil inorganic carbon (SIC) to the changed soil pH. Using a generalized additive model, we identified the soil depth intervals with the most powerful statistical relationships between changes in soil pH and soil carbon dynamics. Hierarchical responses of SOC and SIC dynamics to soil acidification were found. The results indicate that the changes in soil pH explained the SOC dynamics well by using a non-linear relationship at the soil depth of 0–80 cm (P=0.006), whereas the changes in soil pH were significantly linearly correlated with SIC dynamics at the 100–180 cm soil depth (P=0.015). After a long-term N fertilization in the experimental field, the soil pH value decreased in all three N fertilizer treatments. Furthermore, the declines in soil pH in the deep soil layer (100–200 cm) were significantly greater (P=0.035) than those in the upper soil layer (0–80 cm). These results indicate that soil acidification in the upper soil layer can transfer excess protons to the deep soil layer, and subsequently, the structural heterogeneous responses of SOC and SIC to soil acidification were identified because of different buffer capacities for the SOC and SIC. To better estimate the effects of soil acidification on soil carbon dynamics, we suggest that future investigations for soil acidification should be extended to a deeper soil depth, e.g., 200 cm.

Keywords: soil acidification; deep soil; calcium carbonate; generalized additive model (GAM); agroecosystem; soil organic carbon; soil inorganic carbon

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1 Introduction

Soil acidification is a major global threat to the sustainable development of ecosystems (Rengel, 2003). Changes in soil pH can regulate the soil carbon dynamics (Adams and Adams, 1983; Andersson et al., 2000; Kemmitt et al., 2006; Ahmad et al., 2015) and hence impact the role of soil in carbon sequestration. Soil pH impacts the soil organic carbon (SOC) by regulating microbiological processes (Adams and Adams, 1983), and also affects the soil inorganic carbon (SIC) via chemical processes (Yang et al., 2012, 2015). Although the global SIC stock contributes equally to what the SOC contributes (Lal, 2004), studies were mainly concentrated on the effects of soil acidification on SOC dynamic because of the insensitivity of soil acidification in calcareous soils with high SIC. For example, the regions with high amounts of carbonates in croplands of China had the low changes in soil pH, while significant acidification was found over the entire agricultural system (Guo et al., 2010). Nevertheless, the capacity to buffer soil acidity is undertaken by the loss of SIC (Yang et al., 2012). Therefore, the integrated potential role of lowing soil pH in carbon dynamics can be masked in calcareous soils.

Despite being a natural process (Bolan et al., 2003), soil acidification has been accelerated by the overuse of nitrogen (N) fertilizer over recent decades (Campbell and Zentner, 1984; Bolan et al., 2003; Guo et al., 2010; Meng et al., 2013). Generally, the changes of pH in calcareous soils combined with N fertilizer application mainly involve three processes: (1) biological processes, including the increasing proton (H^+) ions produced from nitrification (Eq. 1) and the decomposition of soil organic matter caused by soil microorganisms (Eq. 2) (Zhao et al., 2016); (2) chemical processes of the decreased H^+ ions caused from the dissolution of SIC (Eqs. 3 and 4), which might contribute to soil CO_2 emissions (Ramnarine et al., 2012); and (3) physical processes of leaching the dissolved inorganic carbon ions (bicarbonate and carbonate) to the groundwater (Li et al., 2015). Therefore, the reduced soil pH induced by N fertilizer application can alter the carbon balance in calcareous soils (Yang et al., 2012) and will accelerate acidification in soils with low SIC (Yang et al., 2012).

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+, \tag{1}$$

$$\text{Organic}C \rightarrow RCOOH \rightarrow RCOO^- + H^+, \tag{2}$$

$$CaCO_3 + H_2O + CO_2 \rightarrow Ca^{2+} + 2HCO_3^-, \tag{3}$$

$$HCO_3^- + H^+ \rightarrow H_2O + CO_2. \tag{4}$$

Two moles of H^+ will be produced when one mole of nitrate is produced in the nitrification processes under aerobic conditions (Bolan et al., 2003). In calcareous soils, these protons will be directly neutralized by the SIC when soil pH is stable (Guo et al., 2010). Under this supposition, lowering pH value in calcareous soils has been proven to lead to a significant decline of soil carbonates in grasslands (Yang et al., 2012) and in farmlands with long-term fertilization (Shi et al., 2012). Soil pH indirectly regulates the SOC dynamics by controlling microbial turnover (Adams and Adams, 1983). Meanwhile, both plant-induced and soil-induced carbon processes (carbon assimilation and decomposition of SOC, respectively) can result in a decline of soil pH value. Relationships (positive, negative and no interaction) between SOC dynamics and soil pH vary largely in different studies (e.g., Adams and Adams, 1983; Andersson et al., 2000; Kemmitt et al., 2006). Therefore, how the soil pH impacts the SOC dynamics still needs to be further evaluated or explored (Karlsson, 2013). Furthermore, experiments of lime additions to overcome soil acidification showed that the carbon in limed soil or the SIC will be released at a short-term interval compared with the carbon derived from the SOC (Adams and Adams, 1983). These results implied that the SIC would react firstly to the increase in the protons compared to the SOC. However, if these implications are correct, interpreting why the topsoil can still contain SIC under continuous proton production is an interest and key question. In addition, soil acidification in the topsoil layer can cause acidification in the deep soil layer via the movement of protons (Rengel, 2003; Li et al., 2016). In calcareous soils, due to lower SOC and higher SIC in the deep soil layer

(Li et al., 2007; Wu et al., 2009), the proton input into the deep soil layer can be expected to induce the loss of SIC with the relative stable soil pH in the deep soil layer.

In this study, we explored the relationships between changes in soil pH and soil carbon dynamics over the soil profile of 0–200 cm through a long-term N fertilization experiment (with crop cultivation) conducted in a dryland agroecosystem, China. We expected that this long-term experiment could regulate the soil pH by applying different N fertilization levels. If the changes in soil pH can regulate the soil carbon dynamics, after a long-term (12-year period) N fertilizer application, the changes in soil pH will be expected to explain the changes in soil carbon dynamics, not the absolute carbon content. Due to the spatial heterogeneity of soil pH and soil carbon over the soil profile, a generalized additive model (GAM) was applied to distinguish the responses of SIC and SOC to soil acidification in the soil profile.

Specifically, we tested three hypotheses. The first hypothesis (H1) states that soil pH value of the deep soil (mineral layer) would decrease to a greater extent than those of the topsoil and subsoil layer. The second and the third hypotheses are two competing hypotheses. The second hypothesis (H2) is that if the responses of SIC and SOC to soil acidification are homogeneous, then the changes in soil pH will have the same effect on SIC and SOC at the same soil depth, e.g., both negative or positive. Alternately, if the responses of SIC and SOC to soil acidification are heterogeneous, for example, more SOC can buffer the effect of increasing acidity (Ritchie and Dolling, 1985), then the deep soil layer with lower SOC would lose more SIC than SOC (i.e., the third hypothesis, H3).

2 Materials and methods

2.1 Study area

The study was conducted at a long-term experimental farmland (34º17′44″N, 108º04′10″E; 524 m a.s.l.) of the Northwest A&F University, Yangling, Shaanxi Province, China. This experimental farmland was established in 2002. This area is situated in a dryland agroecosystem of the Loess Plateau and is characterized by a temperate continental climate with an annual mean temperature of 13°C. The mean annual precipitation is 600 mm, with 60% of the total precipitation occurring from July to September. The soil classification is the Eum-Orthic Anthrosol in the FAO system (Wang et al., 2014).

2.2 Experimental design

The experiment was performed as a complete random block design with a total of nine experimental plots (6.6 m×9.9 m for each plot). A monoculture of winter wheat (*Triticum aestivum*) was planted in this area from 2002 to 2014. The N fertilizer application experiments with three N levels (N0, 0 kg N/(hm^2·a); N120, 120 kg N/(hm^2·a); N240, 240 kg N/(hm^2·a)) were initiated in October 2002. The three N application levels represent the control level (without chemical N application), recommended level (the optimal N fertilizer application rate after a soil test) and projected level (the level that the farmers may apply in the future), respectively. For each plot, the phosphate fertilizer was applied at a rate of 100 kg P_2O_5/hm^2. Superphosphate (P_2O_5>16%) and urea (N>46%) were applied as the phosphate and N, respectively. No potash fertilizer was applied. In early October of each year, all fertilizers in each plot were plowed thoroughly to a soil depth of 30 cm. Then, the winter wheat seeds (150 kg/hm^2) were sown by a machine (after 2006), with 30 rows in each plot. All other field managements were followed the adopted practices locally. Finally, the wheat yield was measured in the mid-June of the following year. The original soil properties at the 0–20 cm soil depth in 2002 (before seeding) can be referred to Wang et al. (2014). Table 1 presents the values of SOC content, SIC content, soil pH and soil bulk density at the depth of 0–200 cm in October 2002. Briefly, soil samples were collected using a soil auger (4 cm in diameter) at an interval of 20 cm depth. SOC content was measured using wet combustion with $K_2Cr_2O_7$; SIC content was measured by the manometric collection of CO_2 evolved with an HCl treatment process; soil bulk density was measured using the oven-dry method to the soil mass and the core volume; and soil pH was measured using a pH

meter (PHS-3C) on a 1:5 soil:water extract.

Table 1 Basic soil properties at the depth of 0–200 cm in 2002 (before seeding)

Soil depth (cm)	SOC content (g/kg)	SIC content (g/kg)	Soil pH	Soil BD (g/cm^3)
0–20	11.76	10.66	8.41	1.21
20–40	7.82	11.55	8.18	1.56
40–60	4.48	9.32	8.58	1.48
60–80	3.71	5.66	8.75	1.43
80–100	3.73	1.45	8.50	1.36
100–120	4.22	1.05	8.81	1.36
120–140	4.02	1.73	8.80	1.36
140–160	3.56	8.51	8.86	1.36
160–180	2.89	7.02	8.86	1.36
180–200	2.67	22.73	8.48	1.36

Note: SOC, soil organic carbon; SIC, soil inorganic carbon; BD, bulk density.

2.3 Soil sampling and laboratory analysis

For this study, soil sampling was conducted on 25 June 2014, i.e., after 10 d of harvesting. Samples from 0–200 cm depth were collected using a soil auger (4 cm in diameter) at an interval of 20 cm depth. In each plot, three replicate cores were taken from each soil depth and mixed thoroughly as one sample for this depth. Soil samples were then air-dried after removing the roots and other crop residues. The air-dried samples were ground to fully pass through a 2-mm sieve. Then, they were divided into three parts. One part was used to measure soil pH value using a pH meter (PHS-3C) on a 1:5 soil:water extract; one was used to measure soil carbon after being passed through a 0.15-mm sieve; and the last one was stored as a validation sample. Soil carbon was measured using multi N/C 2100 (Analytik Jean, AG, Germany) at the Institute of East China Sea Fishery Research, Chinese Academy of Fishery Sciences. For soil total carbon (STC), 10–20 mg of soil sample was combusted directly. For SOC, soil samples were reacted with 10% HCl to remove the carbonate and were then combusted thoroughly. The difference between STC and SOC was calculated as the SIC. Next, the carbon stock (kg/m^2) was obtained using the carbon concentration (g/kg), bulk density, and the representing soil depth interval.

2.4 Data and statistical analyses

We used a one-way ANOVA to evaluate the effects of long-term N fertilizer application (12 years) on soil pH, SOC, SIC and STC at each soil depth, and a two-way ANOVA to evaluate the effects in relation to soil depths. The significance level was set at 0.05. Furthermore, the changes in soil pH, SOC, SIC and STC during 2002–2014 were represented using boxplots for each soil depth.

Due to the occurrence of negative values of the effects of N fertilization on soil carbon and soil pH, data transformation to explore linear relationships cannot be carried out by using common transformation methods, e.g., square root or logarithmic transformations. Thus, a generalized additive model (GAM) was applied in this study to investigate the relationships of changes in soil pH with changes in SOC and SIC. The GAM uses smoothing curves to illustrate relationships between the response variable and the explanatory variables. In addition, the GAM can also model linear relationships between variables. A general formula for the GAM is shown as follows (Eq. 5):

$$Y_i=a+s(X_i)+\varepsilon_i \quad \varepsilon_i\sim N\,(0,\,\delta^2), \tag{5}$$

where Y_i represents the soil carbon; a is the intercept of the model; $s(X_i)$ is the population smoothing function and can represent trends in soil carbon changes along the soil profile with the partial residuals of smoothing; ε_i is the error of the model; and δ is the standard deviation. This model can also be named as an additive model with one explanatory variable. Then, to explore the responses of soil carbon to the changes in soil pH at different soil depths based on H2 and H3, we tested and evaluated all possible sub-models of GAM by comparing the significance of changes in soil pH and the explained deviance derived from the corresponding sub-model. Sub-model with a

higher explained deviance and a lower P value (P<0.05) was considered to be the best model. The ANOVA was run in R base package (R Development Core Team, 2016). Difference was considered significant at the P<0.05 level. All sub-models were obtained using the mgcv package (Wood, 2017). Moreover, all figures were plotted using the ggplot2 package (Wickham, 2009).

3 Results

3.1 Changes in soil carbon and soil pH over the soil profile

At each soil depth, there were no significant difference in soil pH and soil carbon contents among different N fertilizer application levels (Fig. 1) and N fertilization exhibited no significant effect on both soil pH and soil carbon contents (Table 2), after a long-term (12 years) N fertilization in the experimental field. However, there was a marginally significant effect of N fertilization on soil pH in relation to soil depths after the long-term N fertilization (P=0.058; Table 3). The soil pH value decreased in all three N fertilizer treatments after the long-term N fertilization in the experimental field (Table 3). Although the N fertilization did change the soil carbon stock at the 0–200 cm soil depth, the recommended N fertilizer application rate (i.e., N120) had the highest SOC stock. Meanwhile, the projected N fertilizer application rate (i.e., N240) had the lowest SIC stock.

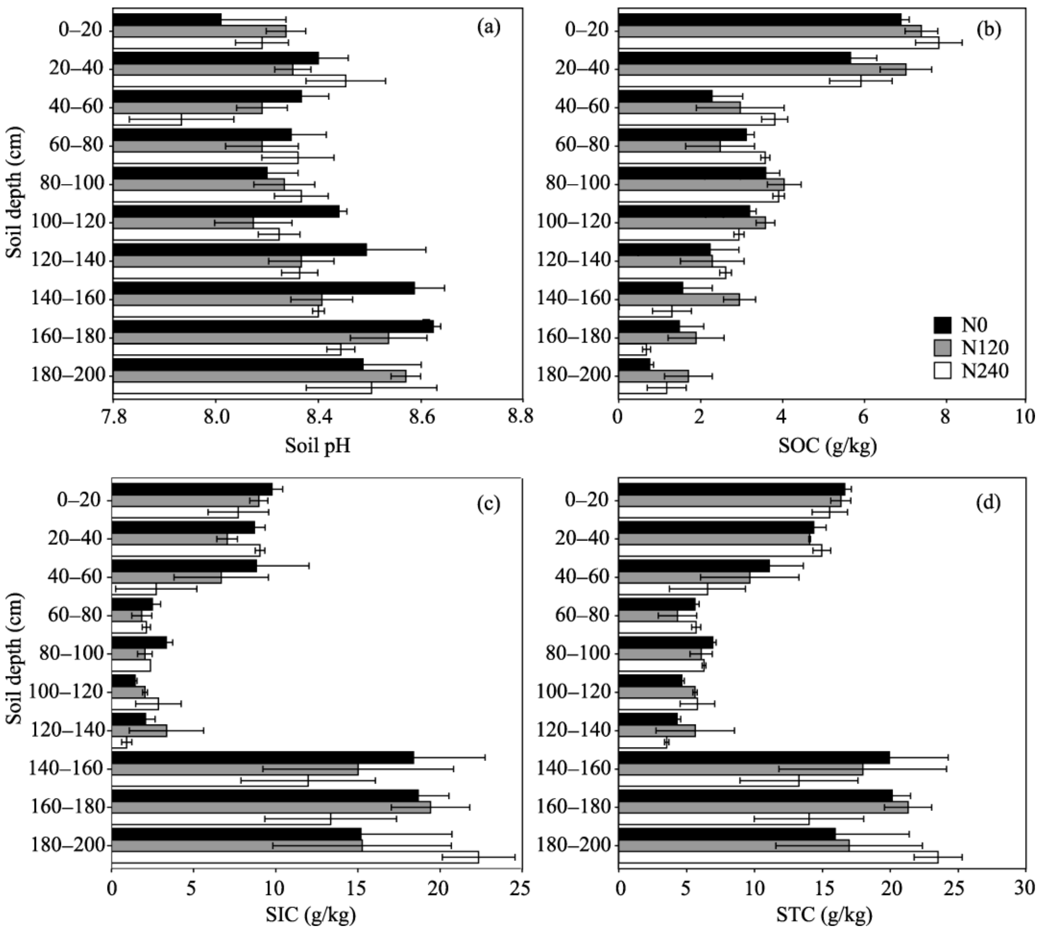

Fig. 1 Vertical distribution of soil pH (a), soil organic carbon (SOC) content (b), soil inorganic carbon (SIC) content (c) and soil total carbon (STC) content (d) at the 0–200 cm soil depth in 2014 under three N fertilizer application levels. N0, N120 and N240 represent the N fertilizer application levels of 0, 120 and 240 kg N/(hm^2·a), respectively. Error bars indicate the standard deviations.

Table 2 Effects (P and F values) of long-term (12 years) N fertilization on soil pH, SOC content and SIC content at each soil depth

Soil depth (cm)	Soil pH		SOC content		SIC content	
	P	F	P	F	P	F
0–20	0.573	0.611	0.359	1.222	0.503	0.772
20–40	0.509	0.757	0.387	1.115	0.086	3.788
40–60	0.145	2.710	0.430	0.974	0.374	1.164
60–80	0.763	0.283	0.359	1.220	0.648	0.467
80–100	0.726	0.338	0.618	0.522	0.078	4.027
100–120	0.131	2.904	0.101	3.435	0.500	0.780
120–140	0.461	0.884	0.895	0.113	0.492	0.799
140–160	0.060	4.658	0.152	2.616	0.662	0.443
160–180	0.104	3.385	0.328	1.352	0.338	1.305
180–200	0.840	0.182	0.670	0.444	0.801	0.235

Table 3 Soil pH change, soil total carbon (STC) stock, SOC stock and SIC stock after a long-term (12 years) N fertilization

N fertilization treatment	Change in soil pH	STC stock (kg/m^2)	SIC stock (kg/m^2)	SOC stock (kg/m^2)
N0	–0.38±0.13	34.02±1.51	25.10±2.44	8.92±0.96
N120	–0.44±0.14	33.21±5.92	22.79±6.16	10.43±1.42
N240	–0.46±0.15	30.48±2.92	20.96±3.11	9.53±0.45
P	0.058	0.544	0.532	0.267

Note: N0, N120 and N240 represent the N fertilizer application levels of 0, 120 and 240 kg N/(hm^2•a), respectively. P values were obtained from the one-way ANOVA. Mean±SD; n=3.

All data were combined to analyze the relationships between changes in soil pH and soil carbon dynamics. The soil pH decreased significantly (mean change value of –0.43; P<0.001) along the soil profile after the long-term N fertilization. For each soil depth, pronounced acidification was found throughout the soil profile (0–200 cm), except for the 20–40 cm soil depth (Fig. 2a). The changes in soil pH after the long-term N fertilization at different soil depths ranged from –0.67 (±0.04) at the 100–120 cm soil depth to 0.01 (±0.03) at the 20–40 cm soil depth. In addition, the amplitude of changes in soil pH after the long-term N fertilization in the topsoil and subsoil layer (0–80 cm) was significantly lower (P=0.035) than that in the deep soil layer (80–200 cm), with the mean change values of –0.36 and –0.48, respectively. This suggests that the effects of N fertilization on soil pH existed the entire soil profile, with a fast response in the deep soil layer.

After the long-term N fertilization, decreases in SOC content were found throughout the soil profile (0–200 cm), except for the 60–100 cm soil depth (Fig. 2b). The topsoil layer lost the most SOC (change of –4.4 (±0.25) g/kg). Obvious changes in SIC content were found throughout the soil profile after the long-term N fertilization, except for the 180–200 cm soil depth (Fig. 2c). Specifically, SIC content was decreased at the 0–80 cm soil depth and increased at the 80–180 cm soil depth. The net change in STC content showed negative values at the 0–100 cm soil depth and positive values at the 100–200 cm soil depth after the long-term N fertilization (Fig. 2d). Generally speaking, the vertical distribution of changes in soil pH was opposite to that of changes in SOC content, while the vertical distribution of changes in SIC and STC contents had similar patterns. This results indicate that potential relationships may exist between soil carbon dynamics and soil acidification.

3.2 Relationships between changes in soil pH and soil carbon content

Given the different distribution patterns of changes in soil pH and soil carbon content, we investigated whether there are significant relationships between changes in soil pH and soil carbon content at different soil depths by comparing their explained deviance and significance value in the sub-models of GAM. The full model comparison is listed in Table 4. The results show that SOC content and SIC content showed different responses to the changes in soil pH. For the

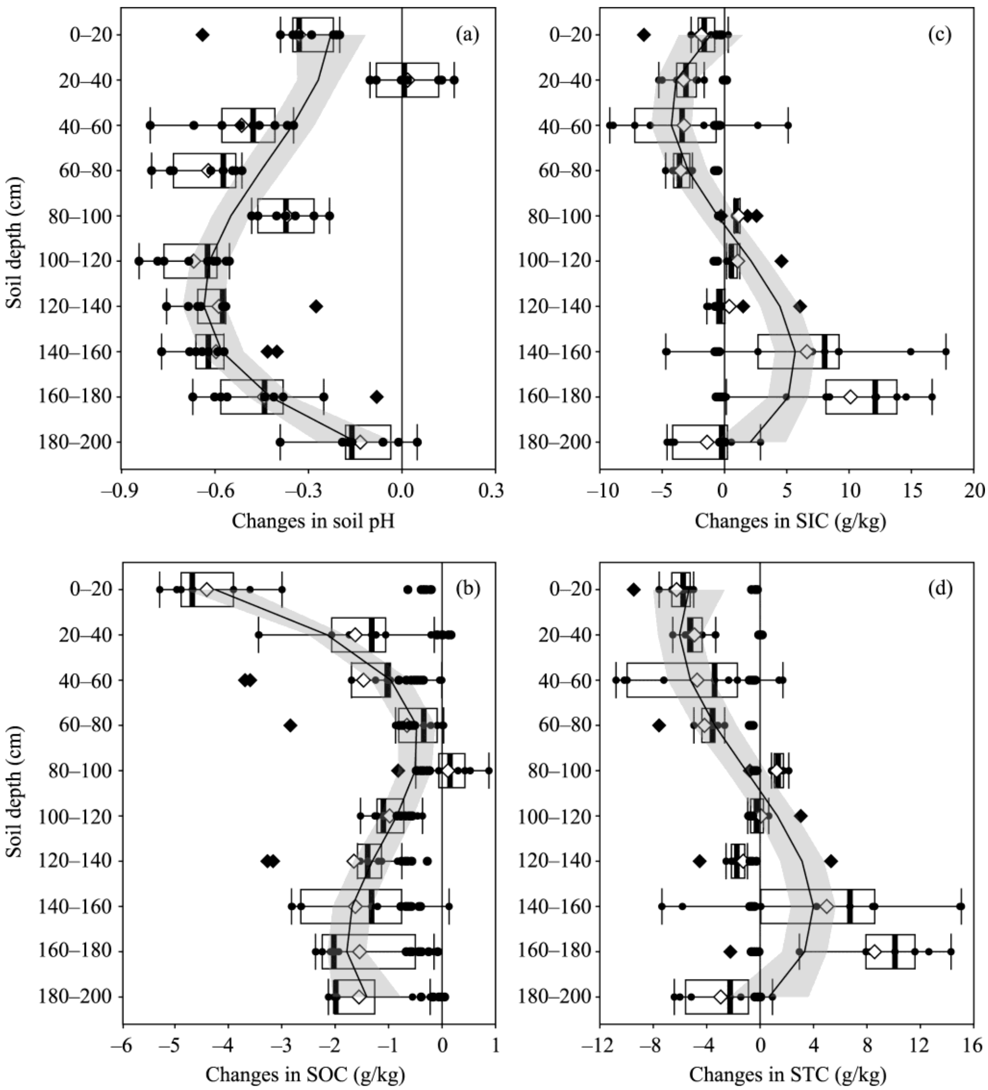

Fig. 2 Changes in soil pH (a), SOC content (b), SIC content (c) and STC content (d) at the soil depth of 0–200 cm after long-term (12 years) N fertilization. The black dot represents the observed value, the white rhombus represents the mean value of the changes, and the black rhombus represents the outlier. The short black solid line within the boxplot represents the median. The left and right whiskers represent the minimum and maximum values, respectively. The zero reference line can conservatively estimate whether significant differences were detected. Significance was considered at the P<0.01 level when the whiskers overlap with the reference line. The estimated trend of changes along the soil profile is shown as a smoothing curve (with one standard error) in the grey region.

optimal relationship between changes in soil pH and SOC content, the changes in soil pH at the 0–80 cm soil depth explained 51.3% of the changes in SOC content (P=0.006; Fig. 3). In contrast, the changes in soil pH at the 100–180 cm soil depth only explained 12.3% of the changes in SOC content (P=0.310). The optimal relationship between changes in soil pH and SIC content was found at the 100–180 cm soil depth (Fig. 3). The changes in soil pH at this depth explained 16.1% of the changes in SIC content (P=0.015). In contrast, the changes in soil pH at the 0–80 cm soil depth only explained 5.5% of the changes in SIC content (P=0.488). These results imply that in calcareous soils, soil acidification will mainly regulate the SOC dynamics in the root layer and the SIC dynamics in the deep soil layer. Furthermore, two piecewise trends for the relationship between soil acidification and SOC dynamics were found. Specifically, when the soil pH decreased by more than 0.2 units, the SOC content would increase significantly; and when the soil

pH decreased by less than 0.2 units, the SOC content would decrease profoundly. For the SIC dynamics, this relationship suggests a nearly linear decline in SIC content with soil acidification.

Table 4 Summary of the R^2, explained deviance and P values in all sub-models using the generalized additive model

Ss (cm)	Es (cm)	Carbon type	R^2	Dev (%)	P	Carbon type	R^2	Dev (%)	P
10	50	SIC	0.023	8.6	0.517	SOC	0.312	46.2	0.092
10	70	SIC	0.014	5.5	0.488	SOC[b]	0.405	51.3	0.006
10	90	SIC	0.126	17.1	0.090	SOC	0.022	4.4	0.164
10	110	SIC	0.004	3.0	0.566	SOC	0.108	18.6	0.175
10	130	SIC	0.008	2.5	0.249	SOC	0.133	20.5	0.091
10	150	SIC	0.027	4.8	0.244	SOC	0.121	18.2	0.076
10	170	SIC	0.034	5.7	0.233	SOC	0.073	13.0	0.202
30	70	SIC	0.000	1.7	0.515	SOC	0.053	9.0	0.129
30	90	SIC	0.183	25.6	0.076	SOC	0.060	9.7	0.200
30	110	SIC	0.010	4.5	0.517	SOC	0.059	9.5	0.189
30	130	SIC	0.013	3.7	0.359	SOC	0.021	4.3	0.249
30	150	SIC	0.032	5.9	0.255	SOC	0.006	2.2	0.248
30	170	SIC	0.052	7.8	0.167	SOC	0.000	0.6	0.515
50	90	SIC	0.247	27.6	0.005	SOC	0.000	1.4	0.562
50	110	SIC	0.020	4.8	0.197	SOC	0.000	1.7	0.453
50	130	SIC	0.000	2.1	0.342	SOC	0.011	7.5	0.714
50	150	SIC	0.000	1.1	0.442	SOC	0.000	0.1	0.828
50	170	SIC	0.040	5.5	0.064	SOC	0.004	2.8	0.559
70	110	SIC	0.037	8.1	0.264	SOC	0.278	37.8	0.067
70	130	SIC	0.044	9.2	0.341	SOC	0.202	29.8	0.112
70	150	SIC	0.000	1.4	0.435	SOC	0.001	1.3	0.458
70	170	SIC	0.052	7.0	0.053	SOC	0.014	3.9	0.374
90	130	SIC	0.029	9.6	0.516	SOC	0.293	41.8	0.087
90	150	SIC	0.000	0.2	0.798	SOC	0.000	2.6	0.343
90	170	SIC	0.020	4.2	0.176	SOC	0.035	6.3	0.221
110	150	SIC	0.013	5.1	0.258	SOC	0.359	45.2	0.019
110	170	SIC[a]	0.137	16.1	0.015	SOC	0.068	12.3	0.310

Note: [a] represents that the soil depth interval of 110–170 cm was selected to describe the best relationship between changes in soil pH and SIC; [b] represents that the soil depth interval of 10–70 cm was selected to describe the best relationship between changes in soil pH and SOC. Ss, the start soil depth of the model; Es, the end soil depth of the model; Dev, explained deviance.

4 Discussion

In this study, we explored the regulation of soil acidification on soil carbon dynamics over a soil profile of 0–200 cm depth in calcareous soils by manipulating a long-term N fertilization experiment. First, we identified that after 12 years of N fertilization, the soil pH over the entire soil profile significantly decreased. Then, we evaluated three hypotheses: the first one (H1) emphasizes the differences in the buffering capacity between soil layers with large amounts of SOC and large amounts of SIC; the second one (H2) highlights the homogeneous responses of soil organic and inorganic carbon dynamics to soil acidification; and the third one (H3) notes the hierarchical responses of soil organic and inorganic carbon dynamics to soil acidification. In conclusion, our results supported the first hypothesis (H1) by implying that the abiotic (deep) soil layer with low SOC content would face more acidity than the biotic (upper) soil layer, and also the third hypothesis (H3) by suggesting that the responses of SOC and SIC to soil acidification are proved to be structurally heterogeneous.

Numerous studies have investigated the effects of N fertilization on soil carbon, yet there is no

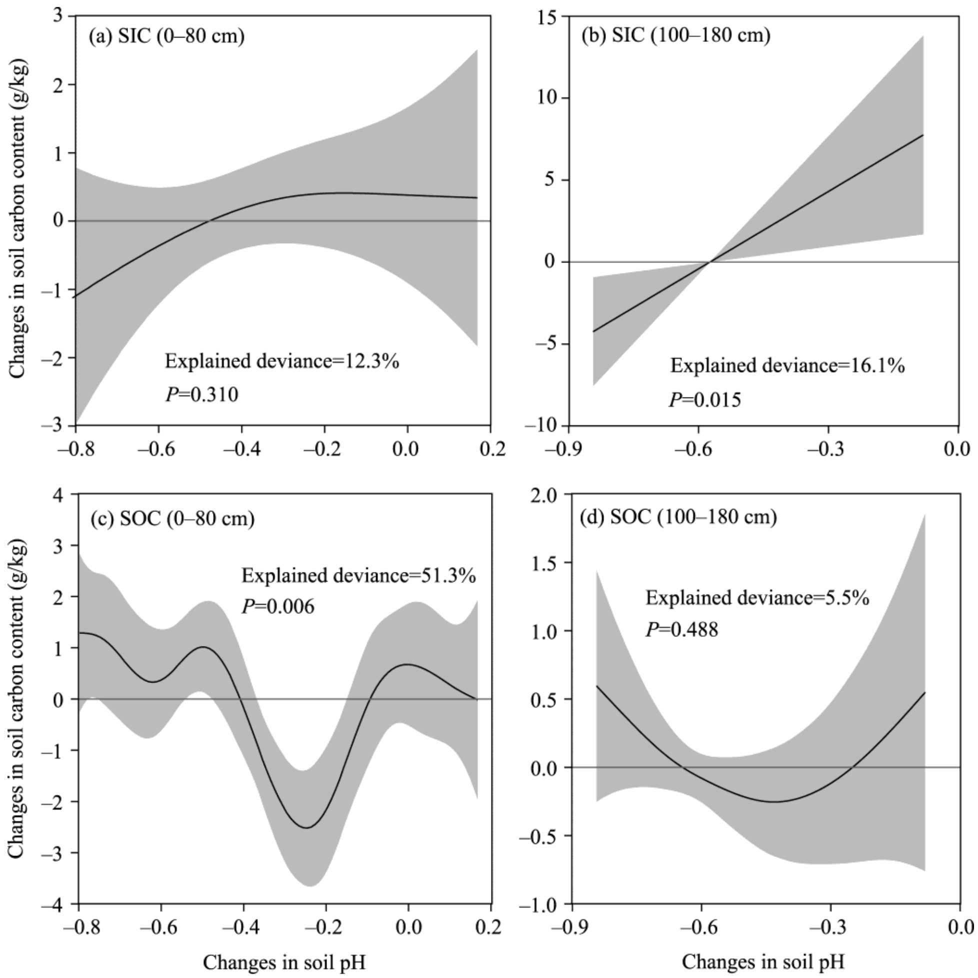

Fig. 3 Optimal relationships between changes in soil pH and SIC content (a, b) and between changes in soil pH and SOC content (c, d) at the 0–80 and 100–180 cm soil depths after model selection. The black solid line represents the spline of the depth, and the grey ribbon represents the 95% confidence interval of the spline.

agreement on these effects (Khan et al., 2007). Marginal differences in soil pH for the effects of N fertilization in our study were similar to the acidification issue on the Loess Plateau, China (Guo et al., 2010). These results indicate the buffering of SIC in the study region. Furthermore, our profile data reveal that the deep soil layer had a greater decline in soil pH than the topsoil and subsoil layer after the long-term N fertilization. This suggests that soil acidification would occur in the deep soil layer than conventional soil observations (Bolan et al., 2003; Rengel, 2003; Iwald, 2016). Previous related studies mostly concentrated on soil layers up to 100 cm depth (Díaz-Hernández, 2010), a depth that was considered as the root depth for most cereal plants (Canadell et al., 1996; Jackson et al., 1996), or up to 30 cm depth (Richter and Markewitz, 1995; Richter and Billings, 2015; Richter et al., 2015). As a result, few studies identified the responses of soil carbon in the deep soil layer to acidification in the upper soil layer. The protons created from the topsoil layer can be moved to the deep soil layer along with irrigation and precipitation (Rengel, 2003). Then, the downward movement of protons leads to a decrease of soil pH value. Furthermore, this also highly implies the role of SOC (contributing less than 20% of the STC) in buffering the soil pH in the deep soil layer (Dong et al., 2013).

In addition, the direct and indirect reaction between soil protons and soil carbon could alter the responses of soil carbon to soil acidification. As expected, there was an almost linear decline in SIC with increasing soil acidity in the deep soil layer in this study. This implies that the loss of SIC would be estimated using a linear function, which is consistent with the empirical regression

function in grasslands and forests (Yang et al., 2012, 2015). However, we did not find the relationships between changes in soil pH and SIC content in the topsoil and subsoil layer. This suggests that other factors may play significant roles in the loss of SIC in the upper soil profile (Curtin et al., 1998). For example, the dissolution of calcium carbonate due to irrigation can contribute up to 60% of CO_2 emissions (Ramnarine et al., 2012; Ahmad et al., 2013). Moreover, the SOC in the regulation of soil pH can also play roles in the loss of SIC in the upper soil layer.

Interestingly, relationships with the high explained deviance were found between changes in soil pH and SOC content. This indicates that soil pH has comparable roles in the regulation of SOC dynamics. The relationships between changes in soil acidity and SOC still remain controversial: positive relationships (e.g., this study; Kemmitt et al., 2006) or negative relationships (Karlsson, 2013). The reason that leads to the controversial relationships might be induced by the indirect effect of soil acidity on soil carbon dynamics. The regulation of soil pH on SOC dynamics can be achieved by controlling the microbial dynamics. Each response during the indirect regulation would affect the ultimate relationships. Moreover, we first applied a nonlinear way to investigate the relationships between changes in soil pH and soil carbon dynamic in this study. The profound decline in SOC content at the beginning of soil acidification (soil pH of 0.0–0.2) may suggest an interesting interaction of microbial dynamics with the increase in soil acidity. However, we do not have any evidence to explain this pattern currently. Then, following the higher acidity in the topsoil and subsoil layer, the changes in the activities of microbes may cause the accumulation of SOC (Kemmitt et al., 2006). This special relationship highlights that more observations of microbiological responses will be needed in the beginning stage of soil acidification.

5 Conclusions

In this study, through a 12-year field N fertilization experiment in a dryland agroecosystem of China, we explored how the soil carbon responses to the soil pH changes over a soil profile up to a depth of 200 cm. The high acidification in the deep soil layer (>100 cm depth) remarkably suggests that the effects of soil acidification on soil carbon dynamic can spread from the biological soil layer (0–80 cm) to the mineral soil layer (>80 cm). The mineral soil layer can directly buffer the excess protons by the linear loss of SIC; in contrast, complex processes can buffer the effects of soil acidification in the biological soil layer. Therefore, to better estimate the comprehensive effects of soil acidification on soil carbon dynamics, we suggest that investigations of soil acidification should be extended to a deeper soil depth, e.g., 200 cm, rather than limited in biological soil depth (<80 cm).

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